

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for the Desulphurization of Aromatic Feedstocks

We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Finsbury Circus, London, E.C.2, a company incorporated in accordance with the Laws of England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the desulphurisation of aromatic feedstocks.

Fractions consisting of or containing aromatic hydrocarbons may be obtained from petroleum hydrocarbon feedstocks or by the destructive distillation of coal. Such fractions are frequently contaminated with sulphur in a number of combined forms, and whether the fraction is to be used as such or is to be further processed it is usually necessary to remove this sulphur. This course is particularly necessary when the fraction is to undergo catalytic conversion over a sulphur-sensitive catalyst. An important case where desulphurisation of an aromatic material is necessary is that in which benzene is obtained, either from a petroleum feedstock by distillation and extraction procedures, or from coal, and then is hydrogenated over a nickel-containing catalyst to give cyclohexane. One of the major uses of cyclohexane is as an intermediate in the manufacture of nylon, and for this requirement a high level of purity is required. Nickel catalysts are used because they have good activity at low temperatures and because they are cheap, but they are extremely sensitive to sulphur-containing materials, and especially to thiophenic sulphur. This form of combined sulphur is one which is not as easily removed by conventional hydrocatalytic desulphurisation procedures as is, for example, mercaptan-type sulphur, and since the presence of such sulphur in a hydrogenation feedstock would, in addition to deactivation of the catalyst and the effect this would have on the conversion efficiency, also adversely affect the hydrogen-

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ated material, it is clear that means must be found to remove or reduce the amount of sulphur present before the feedstock is hydrogenated or is otherwise used.

We have found that aromatic materials may be desulphurized over a supported nickel catalyst in such a way that the catalyst has a long life and operating conditions are mild. The technique is particularly suitable for removal of thiophenic sulphur, but since this is the most difficult of all types of combined sulphur to remove, it will also remove other forms of sulphur. If desired, however, and if the feedstock contains a large amount of sulphur, a preliminary catalytic hydro-desulphurisation step may be employed. Hydrogen sulphide, if present, may also be removed in known manner. Such materials, although removable by the desulphurisation technique to be disclosed, would shorten the catalyst life unnecessarily unless removed previously. The present technique can economically remove up to 10 ppm sulphur at up to 290°C.

We have found that for a supported nickel catalyst there is a "threshold" temperature. Above this temperature the catalysts acts as a conventional hydrogenation catalyst in the presence of hydrogen, but below it hydrogenation occurs only to a limited extent. Below the threshold temperature, however, the supported nickel material is capable of absorbing sulphur. The threshold temperature is comparatively low when the supported nickel material is fresh, but as it absorbs sulphur, and thereby becomes sulphided, the threshold temperature increases. The sulphur capacity of the supported nickel increases with increasing temperature, so that by progressively increasing the operating temperature so that this is just below the threshold temperature the full capacity of the supported nickel may be used. The absorption effect is believed to be a massive effect, i.e. it is not merely a surface phenomenon, and the limit of sulphur capacity occurs when the nickel is sulphided in depth. In terms of the

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sulphur:nickel atomic ratio the capacity of a nickel on sepiolite material is 0.06:1 at 100°C, 0.26:1 at 200°C, and 0.46:1 at 250°C. The ultimate sulphur capacity at much higher temperatures may be as high as 1:1. In practice all hydrogenation activity is lost at an average sulphur:nickel atomic ratio of about 0.1:1.

For convenience the term "supported nickel catalyst" has been used, although the effect is not catalytic in the accepted sense of the term. A small amount of hydrogen should be present, however, because it has been found that in its absence a slow de-activation of the catalyst surface occurs. This is not due directly to the presence of sulphur, but it is thought that when ring type sulphur (i.e. thiophenic sulphur) is absorbed, ring splitting occurs with combination of the sulphur with the nickel surface, leaving an unsaturated hydrocarbon fragment. It is postulated that polymerisation of these unsaturated fragments takes place and that consequently the nickel surface becomes blocked. The presence of as little as 3.7×10^{-2} litres of hydrogen (at NTP) per litre of feedstock when desulphurising a benzene feedstock containing 20 ppm thiophenic sulphur is sufficient to prevent this. The process is not one of catalytic hydro-desulphurisation since hydrogen sulphide does not appear at the reactor outlet.

In accordance with the foregoing the invention consists in a process for the desulphurisation of an aromatic feedstock which comprises contacting the feedstock in the presence of hydrogen, with a supported nickel catalyst at a temperature and pressure at which the catalyst has desulphurisation activity, but below that at which it has substantial hydrogenation activity, and progressively increasing the temperature, and, if desired, increasing the pressure, as the catalyst takes up sulphur, the conditions of operation being such that no substantial amount of hydrogen sulphide is produced in the process.

The term "aromatic feedstock" includes feedstocks containing a major proportion of aromatic hydrocarbons, the remainder of the feedstock being not such as to de-activate the catalyst surface or to be substantially hydrogenated under the reaction conditions, and wholly aromatic fractions or individual hydro-

carbons or mixtures of such hydrocarbons not obtainable by distillation. The term "aromatic hydrocarbons" includes substituted aromatic hydrocarbons in which the substituent group or groups is not such as to be substantially hydrogenated under the reaction conditions or cause de-activation of the catalyst surface. Thus, suitable materials for treatment by the process of the invention would be, for example, mixtures of aromatic hydrocarbons and paraffins or naphthenes, or a single hydrocarbon, such as benzene.

The supported nickel catalyst used may be elemental nickel supported on a natural or synthetic support, such as, for example, a refractory oxide of Groups II to V of the Periodic Table, or kieselguhr, pumice, or sepiolite. Sepiolite is the preferred support. It is a commercially available clay mineral which occurs naturally, and may also be prepared synthetically. Our British Patent No. 899652 discloses and claims catalysts comprising nickel supported on a base consisting essentially of sepiolite, and high surface area (and hence high activity) and high selectivity materials prepared and activated according to the disclosures of this patent are the preferred catalysts for use in the present process. Preferred catalysts contain from 1 to 50% nickel (expressed as elemental nickel), and more particularly from 5 to 25% wt.

The hydrogen used in the present process may be commercially pure, or it may be used as a mixture with one or more substantially sulphur-free reaction-inert constituents. A suitable mixed gas would be that obtained from a steam reformer, containing 95% hydrogen, the remainder of the gas being methane. Gases containing hydrocarbons having two or more carbons per molecule may be used, provided that reaction conditions are carefully controlled to avoid cracking, which in the presence of the nickel catalyst might lead to an exothermic reaction and a temperature runaway. Preferably when inert constituents are present the hydrogen content of the mixed gas should be at least 50 mole %, and more particularly from 70 to 99 mole %.

Suitable operating conditions for the desulphurisation of an aromatic feedstock according to the invention may be selected from the following:

Temperature °C.	progressively increased within the range 50 to 290° C. (122 to 554° F.) corresponding to a sulphur : nickel atomic ratio of 0.035 to 0.53. The preferred range is 75 to 250° C. (167 to 482° F.) corresponding to a sulphur : nickel atomic ratio of 0.045 to 0.46.
Pressure psig	0 to 2000, preferably 0 to 50 up to a sulphur : nickel atomic ratio of 0.1 : 1, and then 50 — 2000.
Space velocity v/v/hr.	0.05 to 10.0 (preferably 0.2 to 5.0).
Inlet hydrogen: molar hydrocarbon ratio on total feed	0.01 to 0.5 : 1 (preferably 0.05 to 0.2 : 1)

In actual operation the reaction pressure may be increased stepwise, since it has been found that this increases the extent of desulphurisation at a given temperature. However, it also increases the extent of hydrogenation taking place at that temperature, and therefore lowers the threshold temperature. The process is carried out, when using a fresh catalyst, by passing the feedstock over the catalyst at a temperature and pressure close to the lower limits of the ranges given above, at which it is known that hydrogenation will not occur to an extent sufficient to cause an unacceptable temperature rise. The sulphur content of the effluent from the process, and its naphthene content, are surveyed and when the sulphur content increases to above a set level the temperature, and, if desired, the pressure, are increased to such an extent that the set value is attained. If the naphthene content increases above the desired level, the temperature and, optionally, pressure, need to be reduced. The actual values of temperature and pressure are, accordingly, compromise values.

Although operation below the threshold temperature means that sulphur absorption is by far the main reaction occurring, some hydrogenation of the feedstock does occur, and this may be an exothermic reaction. Thus in the case of benzene hydrogenation, a temperature rise of 28°F may occur for each one percent conversion to cyclohexane at 440°F.

The degree of hydrogenation that occurs in the present desulphurisation will normally be less than 5% by wt. of the feedstock, but it may be desirable to cool the reactor in which the desulphurisation reaction takes place. This may be done by using recycle of effluent to the reactor inlet or a cooled tubular reactor. The former is preferred, since it allows additional catalyst capacity to be conveniently provided, and is cheaper in capital cost than a tubular reactor. The reaction may be carried out in liquid or gas phase, and in one or more reactors, provided that if more than one reactor is used, reaction conditions in each are identical.

The desulphurised product of the present process may be hydrogenated over a suitable catalyst, such as a nickel or platinum hydrogenation catalyst. A process for the hydrogenation of benzene containing less than 1 ppm sulphur to cyclohexane using two hydrogenation stages is disclosed in our copending British Patent Application No. 28767/65 (Serial No. 1144495). The present desulphurisation process may be used to obtain benzene having less than the above amount of sulphur, and the hydrogenation process of this copending Application preferably uses nickel on sepiolite as the catalyst in each stage.

The invention is illustrated by the following example.

EXAMPLE

Benzene containing 1.3 ppm weight of sulphur was desulphurised over nickel on sepiolite catalyst under the following conditions:—

Pressure psig	3
Temperature °F.	150
Space velocity v/v/h	1.0
Inlet gas	Hydrogen
Inlet H ₂ : hydrocarbon ratio molar	0.1 : 1

Under these conditions 5 per cent weight of benzene was converted to cyclohexane, and the sulphur content of the product was 0.6 ppm weight. However, the extent of the hydrogenation gradually decreased and the sulphur content of the product increased. Consequently, the temperature was raised to improve the desulphurisation efficiency. The effect of the changes in operating temperature was as follows. 10

HOS	Temperature °F.	Cyclohexane Content of Product % wt.	Sulphur Content of Product ppm wt.	Catalyst Sulphur : Nickel Ratio Atomic
0	150	5.1	0.6	0
500		1.3	0.9	0.0015
620	300	2.3	0.5	0.0019
800		1.2	0.6	0.0027
At this point the plant pressure was raised to 15 psig and the levels of hydrogenation and desulphurisation also increased.				
836	300	7.6	0.4	
1420		4.2	0.5	0.0054
1920		3.5	0.8	0.0072
As the activity of the catalyst declined further the temperature was again raised, and it was also possible to increase the pressure to 45 psig.				
2000	400	3.2	0.5	
2380		2.8	0.5	0.003

WHAT WE CLAIM IS:—

1. A process for the desulphurisation of an aromatic feedstock which comprises contacting the feedstock in the presence of hydrogen, with a supported nickel catalyst at a temperature and pressure at which the catalyst has desulphurisation activity, but below that at which it has substantial hydrogenation activity, and progressively increasing the temperature and, 15

if desired, increasing the pressure, as the catalyst takes up sulphur, the conditions of operation being such that no substantial amount of hydrogen sulphide is produced in the process. 25

2. A process as claimed in claim 1, in which the feedstock is either benzene or benzene in admixture with a minor proportion of material, other than sulphur-containing material which is not substantially hydrogenated under the 30

reaction conditions and which does not deactivate the catalyst surface under those conditions.

5 3. A process as claimed in either of the preceding claims in which the supported nickel catalyst is nickel or sepiolite.

10 4. A process as claimed in claim 3, in which the catalyst contains from 1 to 50% wt. nickel expressed as elemental nickel, and preferably from 5 to 25% wt. nickel, by weight of total catalyst.

15 5. A process as claimed in any of the preceding claims in which the reaction temperature is increased within the range 50 to 290°C. and preferably within the range 75 to 250°C.

6. A process as claimed in any of the preceding claims in which the reaction pressure is increased within the range 0 to 2000 psig.

20 7. A process as claimed in claim 6, in which the pressure is from 0 to 50 psig when the catalyst sulphur:nickel atomic ratio is not more than 0.1:1 and from 50 to 2000 psig when the sulphur:nickel atomic ratio is greater than 0.1:1.

8. A process as claimed in any of the preceding claims, in which the space velocity is from 0.05 to 10 v/v/hr, and preferably 0.2 to 5.0 v/v/hr, and the inlet hydrogen:hydrocarbon mole ratio on total feed is 0.01 to 0.5:1, and preferably 0.05 to 0.2:1.

9. A process as claimed in any of the preceding claims, in which a mixed gas containing hydrogen and one or more reaction-inert constituents is used.

10. A process as claimed in claim 9, in which a gas containing approximately 95% hydrogen, together with methane, is used.

11. A process for the desulphurization of an aromatic feedstock substantially as hereinbefore described with reference to the Example.

12. A desulphurised aromatic feedstock, when desulphurised according to a process claimed in any of the preceding claims.

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